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NATURAL CONVECTION AT MICROELECTRODES

by

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NATURAL CONVECTION AT MICROELECTRODES

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Abstract. Steady-state voltammetric currents for $\text{Fe}(\text{CN})_6^{4-}$ oxidation and $\text{Fe}(\text{CN})_6^{3-}$ reduction in 0.2 M KCl solutions are shown to be a function of the orientation of Au and Pt microdisk electrodes (radius = 6.4 to 25 μm) with respect to the gravitational field. The observed angular dependencies for the $\text{Fe}(\text{CN})_6^{3-/4-}$ couple are in agreement with theoretical expectations based on electrochemically-generated fluid density gradients within the depletion layer. The results demonstrate that steady-state voltammetric currents measured at microelectrodes are comprised of both diffusional and natural convection mass-transfer fluxes. At 25 μm -radius microdisks, natural convection accounts for between 2 and 15% of the total current for redox concentrations between 10 and 500 mM, respectively. The contribution of mass-transfer due to natural convection is shown to rapidly decrease with decreasing electrode size.

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Introduction. A key advantage of using microdisk electrodes in electrochemical studies is the rapid attainment of true steady-state response on time scales that are convenient to voltammetric investigations. For a reversible reaction limited only by diffusional transport of reactants, a steady-state voltammetric response can be obtained at a 1 μm -radius electrode at scan rates of ~ 20 mV/s or less,¹ a consequence of the radially-convergent flux of the reactant to the electrode surface.² Analyses of the steady-state voltammetric response assuming diffusional transport greatly simplifies measurements of electrochemical kinetic and transport parameters, as well as providing a conceptually-simple basis for a variety of chemical analyses.

Beginning with the earliest reports of microelectrode investigations,³ it has been generally assumed that natural fluid convection does not contribute to the flux of a redox species, or otherwise influence the steady-state voltammetric response of a microelectrode. Mass transfer due to natural convection, however, occurs in electrochemical measurements whenever the overall reaction yields a product species which induces a change in the solution density near the electrode surface. Electrochemically-generated density gradients near an electrode surface are primarily due to the difference in the charges of the electrochemical reactant and product (and associated counterions), which can alter the structural parameters of the fluid. For instance, an aqueous 15 mM $\text{K}_4\text{Fe}(\text{CN})_6$ solution has a $\sim 0.08\%$ higher fluid density than the corresponding $\text{K}_3\text{Fe}(\text{CN})_6$ solution,⁴ reflecting the fact that the more highly-charged anion ($\text{Fe}(\text{CN})_6^{4-}$), and the larger number of solvated, charge-balancing cations (K^+), cause a decrease in the molar volume of the solution. The difference in the fluid density of the bulk solution (at a distance far from the electrode surface) and that of the diffusion layer creates a net buoyancy force that induces natural convective flow of the solution.⁵ Voltammetric limiting currents may be significantly increased, if natural convection results in transport of the redox species at rates comparable to that of diffusion.

It is well known that natural convection at large electrodes (e.g., 0.1 cm² electrode area) can be significant for measurements made on long time-scales.⁶ Indeed, the development of transient electrochemical methods (e.g., chronoamperometry) is due in part to the desire to obtain data free of the interfering effects of natural convection. The general assumption that natural convection has a negligible effect on the steady-state response of a microelectrode is based on the following arguments. First, because of the radially-convergent flux of a redox species to a microdisk electrode, the rate of diffusional transport can be orders of magnitude larger than that attainable at a planar electrode. Consequently, other modes of transport (i.e., convection) should be masked by the large diffusional contribution.⁷ This argument does not preclude the occurrence of natural convection, but rather simply states that it is of less importance as the dimensions of the electrode are decreased. Second, as the electrode dimensions are reduced, the effects of convective fluid flow on mass-transport to microelectrodes should be greatly reduced due to the fact that the solution velocity profile must decay to zero at a solid surface (i.e., the "no-slip" boundary condition). Consequently, the largest fluid velocities due to the density-driven buoyancy force must occur at a distance located at a finite distance from the electrode surface. Thus, as the electrode dimensions are reduced, natural convection should have a less pronounced effect on the concentration profiles of redox species near the electrode surface.

For a reversible electrochemical reaction, the steady-state limiting current at a microdisk is given by⁸

$$i_{lim} = 4nFDr_0C^* \quad (1)$$

where n = number of electrons transferred, F is the Faraday, D is the diffusion coefficient, r_0 is the electrode radius, and C^* is the bulk redox concentration. Eq. (1) is derived based on the assumption that the redox species is transported to the electrode surface solely by diffusion, without influence of migration or convective transport. Neglecting the migrational flux has been demonstrated to be a valid assumption in solutions

containing an excess concentration of an inert supporting electrolyte.^{2,9,10} In contrast, to our knowledge, the validity of the assumption that i_{lim} is not influenced by natural convection has not been rigorously tested by either experiment or theory. However, in cases where accurate values of the diffusion coefficient can be obtained from independent measurements, voltammetric measurements using carefully prepared microelectrodes in unstirred solutions yield currents that are in reasonable agreement (~5%) with predictions made using eq. (1).

In the present report, we describe a relatively simple experiment that allows the contribution of natural convection to be precisely measured from the steady-state limiting current (i_{lim}) at microelectrodes. Our experiments are based on measuring the dependence of i_{lim} on the orientation of the electrode with respect to the earth's gravitational field. An increase in i_{lim} due to natural convective flow is readily measurable for redox concentrations as low as 10 mM.

Experimental. Au (6.4 μm radius) and Pt (12.5 and 25 μm radius) microdisk electrodes were constructed by sealing Au or Pt wire in glass tube. Electrodes were polished using 0.1 μm Al_2O_3 , rinsed with H_2O , and sonicated in H_2O for ~2 minutes to remove polishing debris.

A standard three-electrode cell containing a Ag/AgCl reference electrode, Pt wire counter electrode, and a Au or Pt microelectrode was used throughout this study. The microelectrode was inserted horizontally (Fig. 1) into the cell through a leakproof port. A 90° bend in the glass tubing encasing the microelectrode was made to facilitate studies of the dependence of the voltammetric response on the orientation of the microelectrode with respect to the earth's gravitational field. Rotation of the electrode, as shown in Fig. 1, allowed the angle θ between the gravitational field, g , and the electrode surface normal, \hat{n} , to be conveniently varied over 360°. The angle $\theta = 0^\circ$ corresponds to the electrode facing

downward (i.e., \hat{n} and g in the same direction). Measurements were made with the cell positioned on a lab bench without attempt to isolate vibrations.

$K_4Fe(CN)_6 \cdot 3H_2O$ and $K_3Fe(CN)_6$ (Mallinckrodt, AR grade) were used as received. H_2O was purified using a Barnstead "E-pure" purification system.

Results and Discussion.

Dependence of i_{lim} on Electrode Orientation.

Fig. 2 shows the voltammetric response of a 25 μm radius-Pt disk electrode in aqueous solutions containing either 0.5 M $Fe(CN)_6^{4-}$ or 0.5 M $Fe(CN)_6^{3-}$. All solutions described throughout this report contained 0.2 M KCl as an inert supporting electrolyte. The sigmoidal-shaped voltammograms correspond to the 1-e⁻ oxidation of $Fe(CN)_6^{4-}$ and the 1-e⁻ reduction of $Fe(CN)_6^{3-}$. In each case, three voltammograms are shown which correspond to electrode orientations of $\theta = 0^\circ$, 90° , and 180° , relative to the earth's gravitation field. As seen in Fig. 2, the limiting current for the oxidation of $Fe(CN)_6^{4-}$ increases in the order $i_{lim}(90^\circ) > i_{lim}(180^\circ) > i_{lim}(0^\circ)$. For the reduction of $Fe(CN)_6^{3-}$, the angular dependence is different and follows the order $i_{lim}(90^\circ) > i_{lim}(0^\circ) > i_{lim}(180^\circ)$. The magnitude of i_{lim} (between 3.0 and 3.7 μA) is in good agreement with theoretical expectations^{10,11} assuming diffusion coefficients for $Fe(CN)_6^{4-}$ and $Fe(CN)_6^{3-}$ of $\sim 7 \times 10^{-6} \text{ cm}^2/\text{s}$. The voltammograms shown in Fig. 2 are reproducible within the penwidth of the voltammetric trace.

The complete dependencies of i_{lim} on θ for $0^\circ < \theta < 360^\circ$ are shown in Fig. 3 as plots of $(i_\theta - i_0)/i_0$, where $i_\theta = i_{lim}$ measured at an arbitrary angle θ and $i_0 = i_{lim}$ measured at $\theta = 0^\circ$. The quantity $(i_\theta - i_0)/i_0$ represents a normalized limiting current, which is particularly useful for comparing the magnitude of natural convection on other experimental parameters (e.g., concentration of redox species and electrode radius). Fig. 3 clearly shows that the minimum value of i_{lim} for $Fe(CN)_6^{4-}$ oxidation occurs at $\theta = 0^\circ$, while the minimum value of i_{lim} for $Fe(CN)_6^{3-}$ reduction occurs at $\theta = 180^\circ$. In both cases, the

maximum value of i_{lim} occurs when the electrode is oriented in the vertical position (i.e., at $\theta = 90^\circ$ or 270°). The observed behavior can be readily explained as follows.

Oxidation of Fe(CN)_6^{4-} results in a solution near the electrode that is comprised of both Fe(CN)_6^{4-} and Fe(CN)_6^{3-} , as well as a decrease in the number of charge-balancing K^+ cations. Since $\text{K}_4\text{Fe(CN)}_6$ solutions have a slightly higher density than $\text{K}_3\text{Fe(CN)}_6$ solutions,^{12,13} it follows that the diffusion layer will have a lower density than the bulk solution during the voltammetric oxidation of Fe(CN)_6^{4-} . In completely analogous fashion, reduction of Fe(CN)_6^{3-} will result in an increase in the solution density within the diffusion layer, relative to that of the bulk solution. When the electrode is oriented at $\theta = 0^\circ$, the reduction of Fe(CN)_6^{3-} will generate a dense diffusion layer that will tend to sink under the influence of the gravitational field, resulting in the flow of fresh solution inwards along the surface of the insulating glass sheath. This natural convective flow results in increased mass-transfer of Fe(CN)_6^{3-} to the electrode surface. Conversely, at $\theta = 180^\circ$, convective flow of the denser diffusion layer will be inhibited by the solid electrode surface, resulting in little (if any) increase in mass-transport. This reasoning explains the observation that $i(\theta = 0^\circ)$ is larger than $i(\theta = 180^\circ)$ for Fe(CN)_6^{3-} reduction. By analogy, oxidation of Fe(CN)_6^{4-} generates a relatively less dense diffusion layer that will tend to rise under the influence of the gravitational field when $\theta = 180^\circ$ (inducing convective flow), but which should be relatively stagnant at $\theta = 0^\circ$ due to the blocking effect of the electrode surface. Thus, $i(\theta = 180^\circ)$ should be larger than $i(\theta = 0^\circ)$ for the oxidation of Fe(CN)_6^{4-} , as is experimentally observed (Fig. 3). For either Fe(CN)_6^{4-} oxidation or Fe(CN)_6^{3-} reduction, the largest limiting currents are observed when the electrode is oriented vertically (either at $\theta = 90^\circ$ or 270°), as is anticipated since the flow profiles of the fluid at these angles are aligned parallel with the direction of the external gravitation force. We note that the variation in $(i_\theta - i_0)/i_0$ for Fe(CN)_6^{4-} oxidation between the vertical (i.e., $\theta = 90^\circ$) and horizontal orientations ($\theta = 0^\circ$) is, within error, equal to the difference in $(i_\theta - i_0)/i_0$ for Fe(CN)_6^{3-} reduction measured at $\theta = 90^\circ$ and $\theta = 180^\circ$.

This result suggests that the rising of the less dense diffusion layer (during Fe(CN)_6^{4-} oxidation) induces the same rate of convective mass-transport as the sinking of a denser diffusion (during Fe(CN)_6^{3-} reduction). The result is in agreement with the expectation that the buoyancy force should be the same for both cases (but in opposite directions).

Effect of Bulk Redox Concentration and Electrode Radius.

Density driven convective mass-transport should decrease as the difference in the density of the bulk solution and depletion layer ($\Delta\rho$) decreases.⁵ This prediction is readily examined by lowering the concentration of the parent redox species in the solution. For instance, Fig. 4 shows plots of $(i_\theta - i_0)/i_0$ vs θ measured in solutions containing between 0.01 and 0.5 M Fe(CN)_6^{4-} . As evident by inspection of this plot, natural convection decreases as the bulk Fe(CN)_6^{4-} concentration is decreased, becoming very small (~2%) at the lowest concentrations investigated (10 mM).

Fig. 5 shows $(i_\theta - i_0)/i_0$ as a function of the electrode radius, r_0 , for the oxidation of 0.5 M Fe(CN)_6^{4-} . As anticipated based on the arguments presented in the *Introduction*, the relative contribution of natural convection to mass-transfer fluxes is greatly diminished as r_0 is decreased. For instance, Fig. 5 shows that the maximum variation in $(i_\theta - i_0)/i_0$ decreases from ~15% to ~1% as r_0 is decreased from 25 to 6.4 μm . We believe this decrease is due to the 4-fold increase in the diffusional flux of the redox species as the electrode radius is reduced from 25 to 6.4 μm , as well as to the reduction of fluid convection within the depletion layer. When employing less concentrated solutions, the effect of electrode orientation on i_{lim} measured at the 6.4 μm -radius electrode is below the detection limit.

Although extensive tabulations of empirical correlations have been compiled for natural convective heat- and mass-transfer, we have not been able to identify one that corresponds to the geometry of an inlaid microdisk shrouded by an insulator. However, reported correlations for heat-transfer at microspherical particles indicate that natural

convection scales approximately as $r_0^{1.75}$ and $\Delta\rho^{1/4}$ and (where $\Delta\rho$ is the difference in the bulk and surface densities).¹⁴ Thus, the effect of natural convection on i_{lim} should be strongly dependent on the microelectrode radius but weakly dependent on the redox concentration. Assuming that the magnitude of the angular dependence of $(i_\theta - i_0)/i_0$ (i.e., the difference in the minimum and maximum values of $(i_\theta - i_0)/i_0$) corresponds roughly to the increase in i_{lim} due to natural convection, the data presented in Figs. 4 and 5 show that mass-transfer by natural convection is indeed strongly dependent on r_0 and weakly dependent on the bulk $K_4Fe(CN)_6$ concentration. For instance, the variation in $(i_\theta - i_0)/i_0$ decreases by a factor of ~ 15 as the electrode radius is decreased from 25 to 6.4 μm , in reasonably good agreement with the predicted value of $(25/6.4)^{1.75} = 10.9$ obtained from the heat-transfer correlation. Using the data in Fig. 4, the maximum variation in $(i_\theta - i_0)/i_0$ increases only by a factor of 3 when the bulk $K_4Fe(CN)_6$ concentration is increased 20-fold (from 0.025 to 0.5 M), slightly larger than the predicted value of $(20)^{1/4} = 2.1$. The differences in the observed and predicted values are most likely due to the approximation made in employing the correlation for a microsphere in predicting the behavior of a microdisk electrode. However, the qualitative trends are in excellent agreement with expected mass-transport behavior resulting from natural convection.

Transient Response.

Fig. 6 shows the angular dependence of the chronoamperometric response ($i-t$) of the 25 μm -radius electrode in 0.5 M $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ solutions. The $i-t$ curves were recorded following a large-amplitude potential step onto the limiting current plateau of the voltammetric wave (see Fig. 2). The $i-t$ response is particularly instructive in measuring the time scale of the onset of measurable effects of natural convection following electrogeneration of the density gradients within the depletion layer. For $Fe(CN)_6^{4-}$ oxidation, we observe that the $i-t$ curves are independent of the electrode

orientation for $t < 2$ s. This observation suggests that mass-transfer of the reactant by natural convection is negligible at short times in comparison to diffusion and migration. However, Fig. 6 shows that the current measured at $\theta = 90^\circ$ or 270° reaches a steady-state response at much shorter times than that observed at $\theta = 0^\circ$ or 180° . Recalling that the increase in mass-transfer due to natural convection is largest for $\text{Fe}(\text{CN})_6^{4-}$ oxidation at $\theta = 90^\circ$ or 270° (as apparent in the angular dependence of the steady-state i_{lim} , Fig. 3), the i - t response clearly indicates that natural convection also significantly increases the rate of attainment of the steady-state for microdisk electrodes. For $\theta = 0^\circ$, where natural convection is anticipated to be minimal due to the blocking of the upward fluid flow by the electrode surface, the i - t response decays with a nearly $t^{1/2}$ dependence as anticipated for a diffusion controlled response. At $\theta = 180^\circ$, the i - t response is more complex, showing a minimum at $t \sim 10$ s, and then an asymptotic approach to steady-state. The minimum in the i - t response at $\theta = 180^\circ$ can be clearly attribute to the $t^{1/2}$ decrease in the diffusional flux being offset after a finite time ($t > 2$ s) by the onset of natural convection.

Analogous chronoamperometric behavior is observed for the reduction of $\text{Fe}(\text{CN})_6^{3-}$ (lower part of Fig. 6). However, the i - t responses measured at $\theta = 0^\circ$ and 180° are reversed relative to that observed for $\text{Fe}(\text{CN})_6^{4-}$ oxidation, due to the fact the buoyancy force acting on the more dense depletion layer is now directed downward. All features observed in the i - t responses for $\text{Fe}(\text{CN})_6^{4-}$ oxidation are observed in the responses for $\text{Fe}(\text{CN})_6^{3-}$ reduction, including a minimum in the i - t response at $t \sim 8$ s when $\theta = 0^\circ$.

The angular dependencies of both the steady-state voltammetric curves and the transient i - t responses suggest that measurements of $\text{Fe}(\text{CN})_6^{4-}$ oxidation are least influenced by the gravitational field when $\theta = 0^\circ$ (i.e., the electrode is oriented horizontally upward). Conversely, measurements of $\text{Fe}(\text{CN})_6^{3-}$ reduction are least affected when $\theta = 180^\circ$. However, it can not be ascertained if the observed currents in either of these limiting cases are completely unaffected by the gravitational field.

Conclusion. The data reported unequivocally demonstrate that natural convection resulting from electrochemically-generated density gradients within the depletion layer can influence mass-transfer limited currents measured at microdisk electrodes. However, we have shown that the relative importance of natural convection decreases rapidly with decreasing redox concentration or the electrode radius. Thus, it is unlikely that natural convection will have a discernible effect in quantitative measurements of low analyte concentrations when using microdisk electrodes. However, it is more likely that natural convection may be important in experiments using microdisks to study homogeneous chemical reactions that are coupled to the initial electron-transfer reaction, and which occur at finite distances from the electrode surface where the convective fluid velocity is largest. In this situation, natural convection may significantly alter the concentration profiles of the reactants, without affecting the measured voltammetric current. Measurements of the electrogenerated concentration profiles using, for instance, scanning electrochemical microscopy¹⁵ or interference microscopy¹⁶, may be able to readily detect this phenomenon.

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 10. Because the redox concentrations (0.5 M) are greater than that of the inert supporting electrolyte (0.2 M), the voltammetric response is not strictly diffusion controlled, but also includes a contribution from ion migration. However, theoretical analysis (ref. 10) indicates that migration has a very small effect on i_{lim} for the solution conditions employed in our study (migration accounts for an ~11% increase in i_{lim} values measured in the 0.5 M redox solutions, and less in all other solutions). Therefore, the effects of migration has been ignored, and eq.(1) has been used to compute approximate values of the diffusion coefficients.
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 12. The density (ρ) of an aqueous solution of $\text{K}_4\text{Fe}(\text{CN})_6$ at a particular concentration is always larger than that of the corresponding $\text{K}_3\text{Fe}(\text{CN})_6$ solution. (See ref. 4 for tabulated values of densities for $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ solutions). In addition, ref. 13 reports values of $\partial\rho/\partial C$ for $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ containing 0.2 M Na_2SO_4 . The value of $\partial\rho/\partial C$ for $\text{K}_4\text{Fe}(\text{CN})_6$ is greater than that of $\text{K}_3\text{Fe}(\text{CN})_6$.

implying that the density of a $\text{K}_4\text{Fe}(\text{CN})_6$ solution containing an supporting electrolyte is also larger than that of the corresponding solution of $\text{K}_3\text{Fe}(\text{CN})_6$. We assume that a similar trend holds for $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ solutions containing KCl as the supporting electrolyte.

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Figure Captions.

1. Schematic of the microelectrode employed in this study. The electrode is inserted horizontally into the cell and rotated about the angle θ (defined by the surface normal, \hat{n} , and the gravitational field, \mathbf{g}). $\theta = 0^\circ$ corresponds to the electrode facing downward.
2. Voltammetric response of a 25 μm -radius Pt disk electrode in (*top*) 0.5 M $\text{K}_4\text{Fe}(\text{CN})_6$ and (*bottom*) 0.5 M $\text{K}_3\text{Fe}(\text{CN})_6$ solutions containing 0.2 M KCl at $\theta = 0, 90$, and 180° . Scans rates are 1 and 2 mV/s for measurements in the $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ solutions, respectively.
3. Angular dependence of normalized limiting current $((i_\theta - i_0)/i_0)$ for $\text{Fe}(\text{CN})_6^{4-}$ oxidation and $\text{Fe}(\text{CN})_6^{3-}$ reduction. All values of i_{lim} were recorded in unstirred solutions containing 0.2 M KCl as the supporting electrolyte.
4. Angular dependence of normalized limiting current $((i_\theta - i_0)/i_0)$ for $\text{Fe}(\text{CN})_6^{4-}$ oxidation as a function of $\text{K}_4\text{Fe}(\text{CN})_6$ concentration. All values of i_{lim} were recorded in solutions containing 0.2 M KCl as the supporting electrolyte.
5. Angular dependence of normalized limiting current $((i_\theta - i_0)/i_0)$ for $\text{Fe}(\text{CN})_6^{4-}$ oxidation as a function of the electrode radius. Data corresponding to $r_0 = 6.4 \mu\text{m}$ were obtained using a Au microdisk. Other data sets were obtained using Pt microdisks. All values of i_{lim} were recorded in solutions containing 0.2 M KCl as the supporting electrolyte.
6. Angular dependence of the chronoamperometric response (i vs. t) of a 25 μm -radius-Pt disk electrode in 0.5 M solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ (*top*) and $\text{K}_3\text{Fe}(\text{CN})_6$ (*bottom*). Both solutions contained 0.2 M KCl as an inert supporting electrolyte.

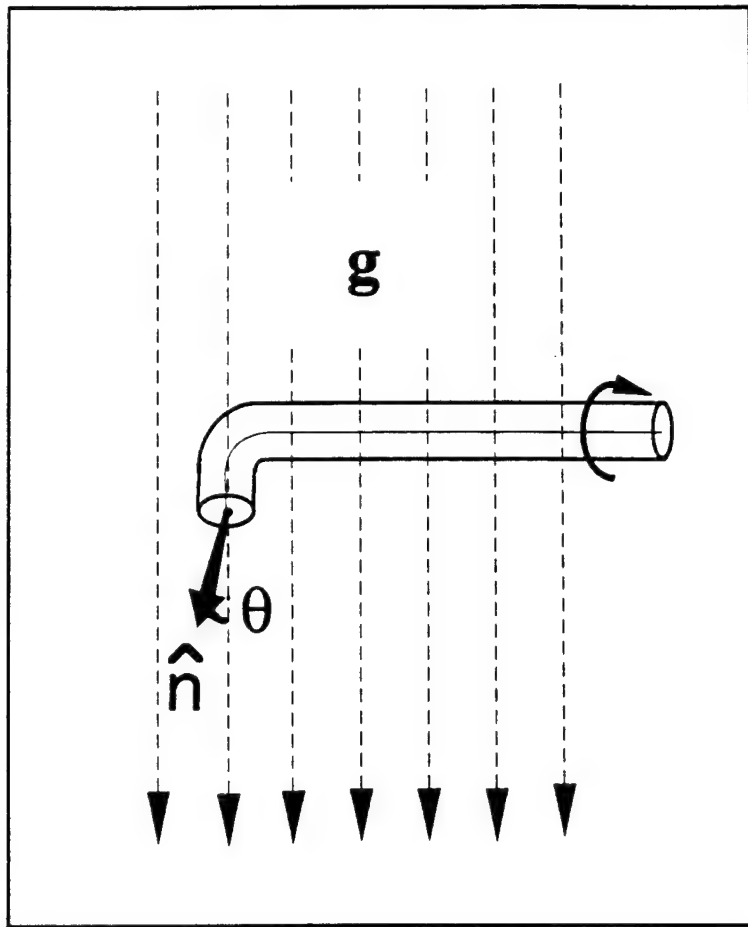


Fig 1

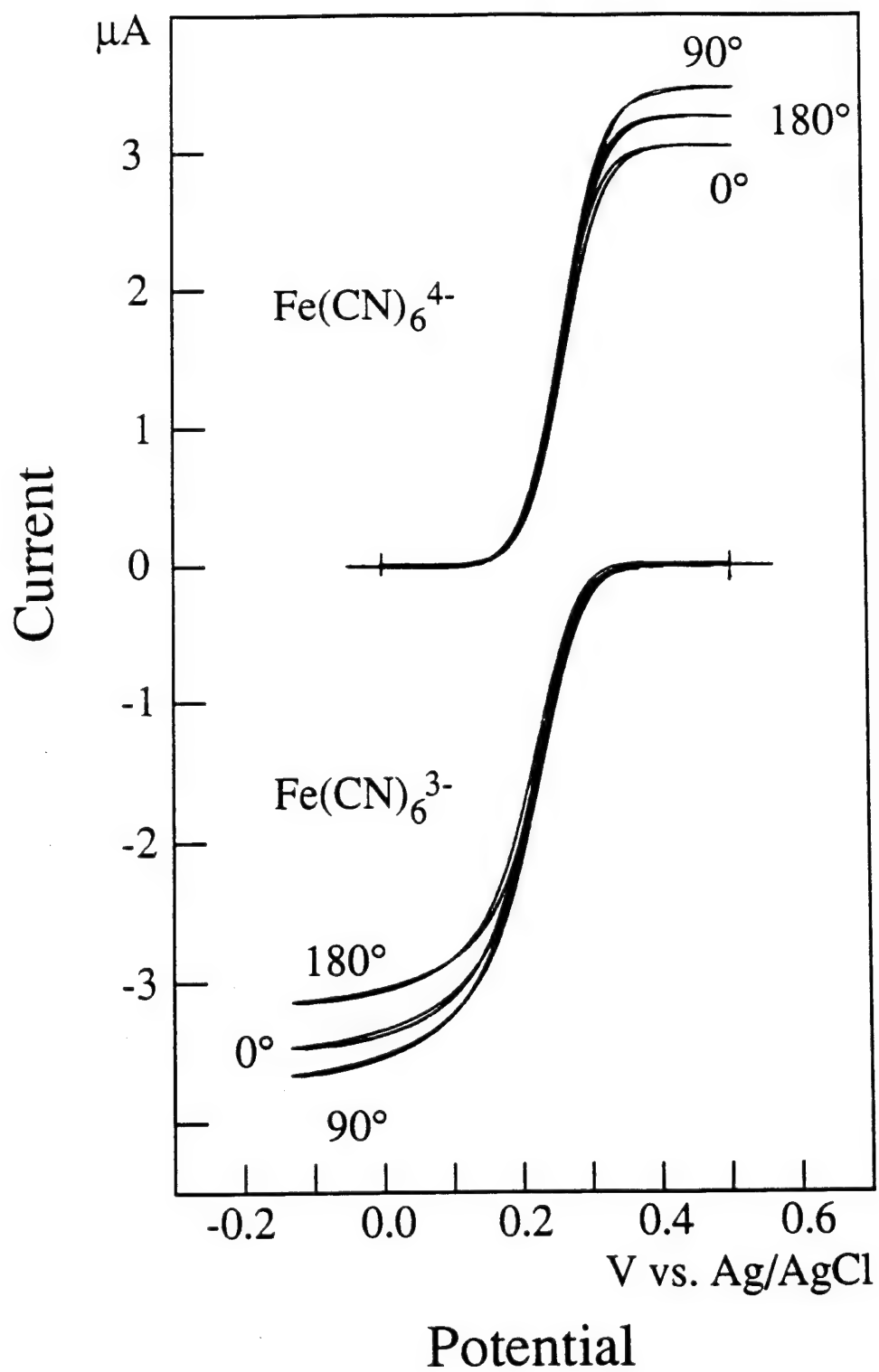


Fig 2

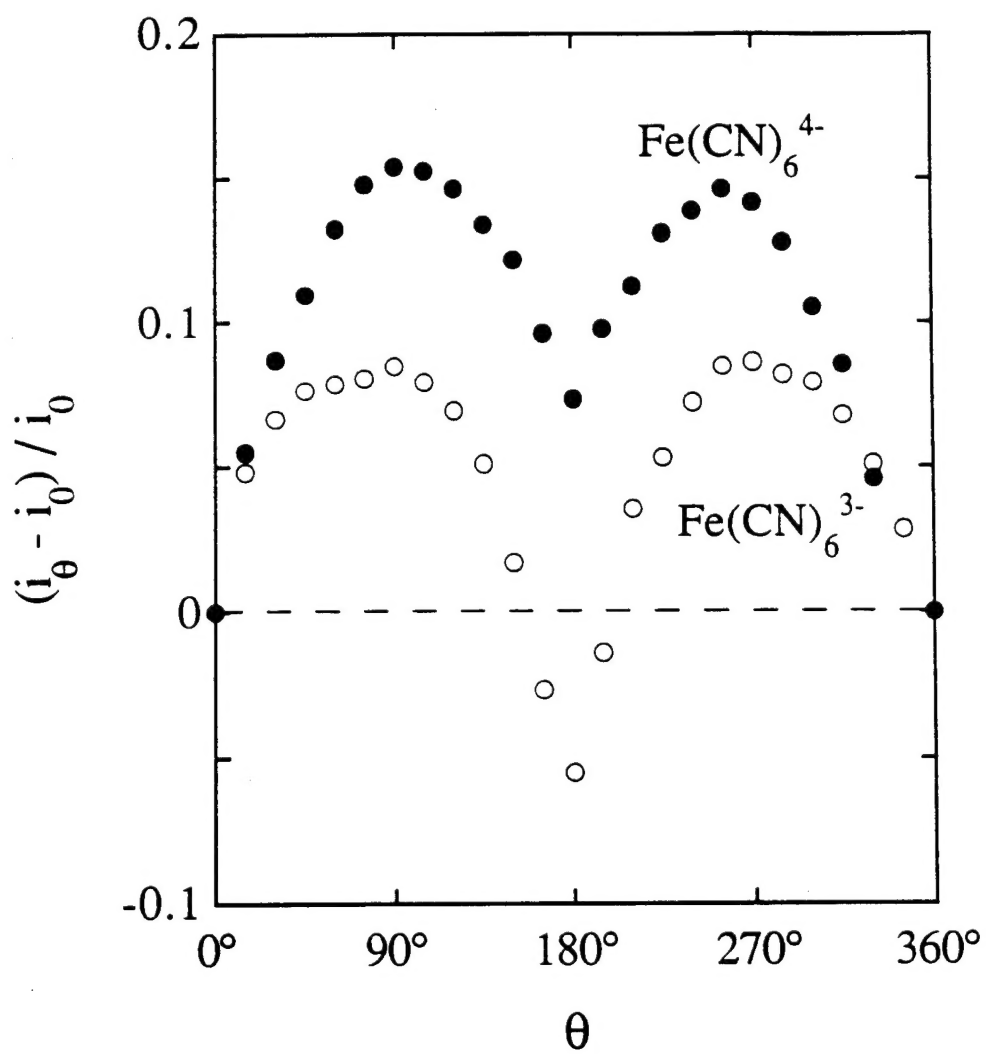


Fig 3

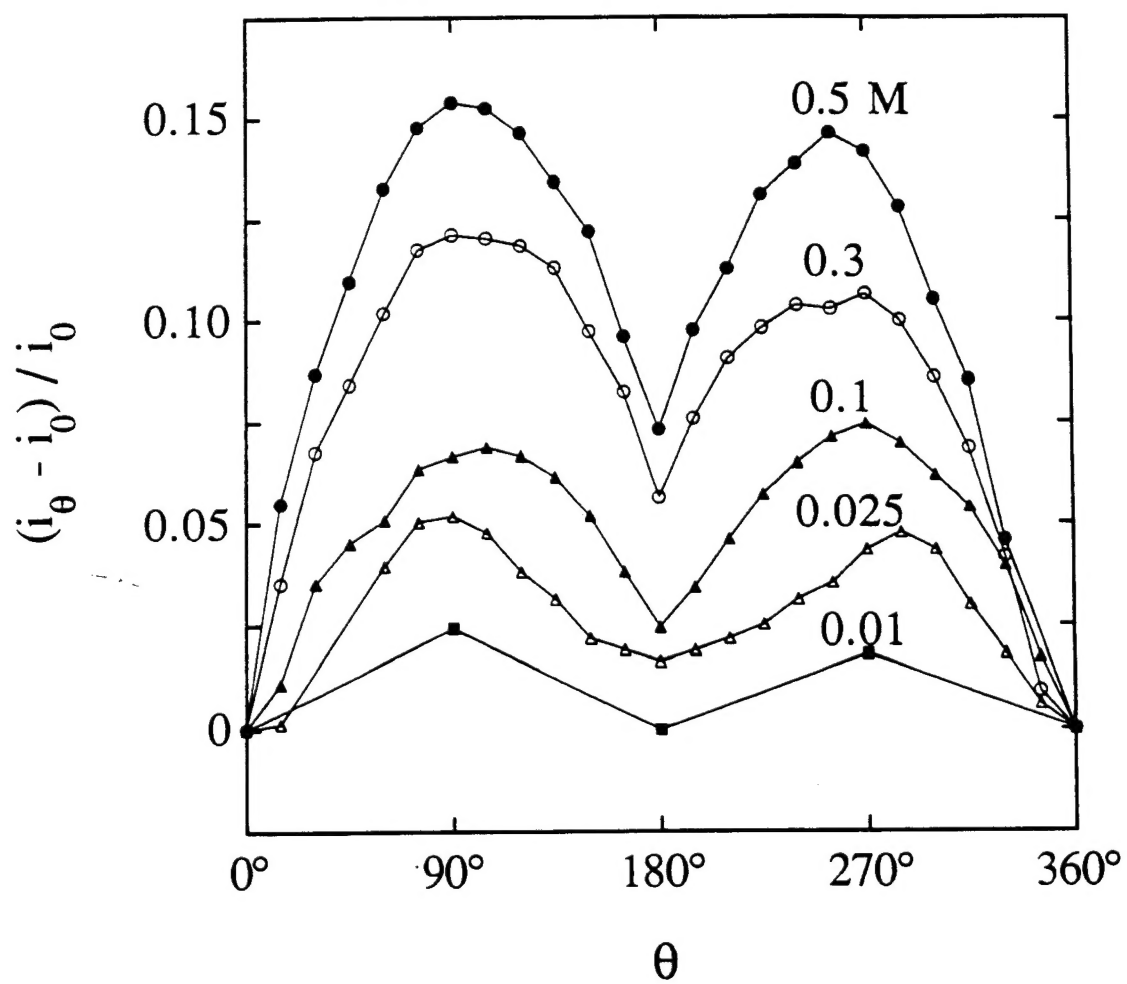


Fig 4

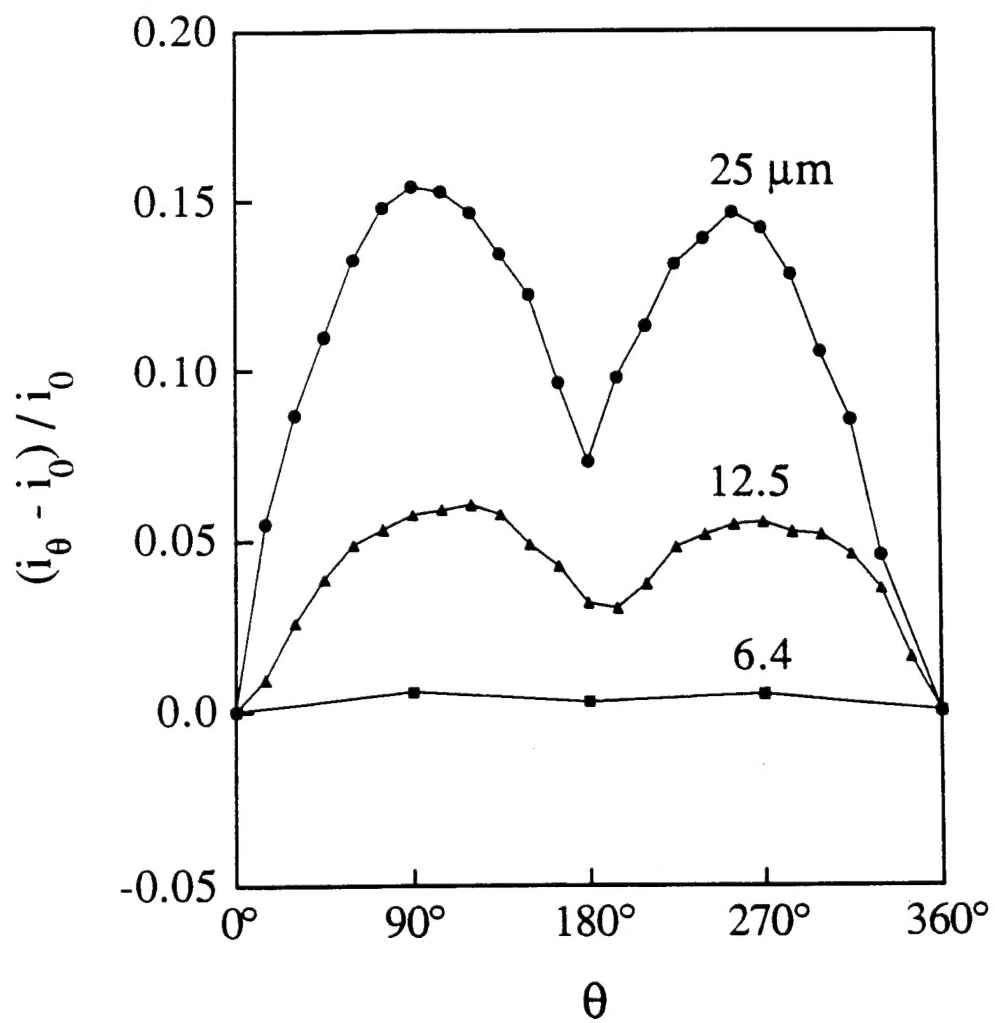


Fig 5

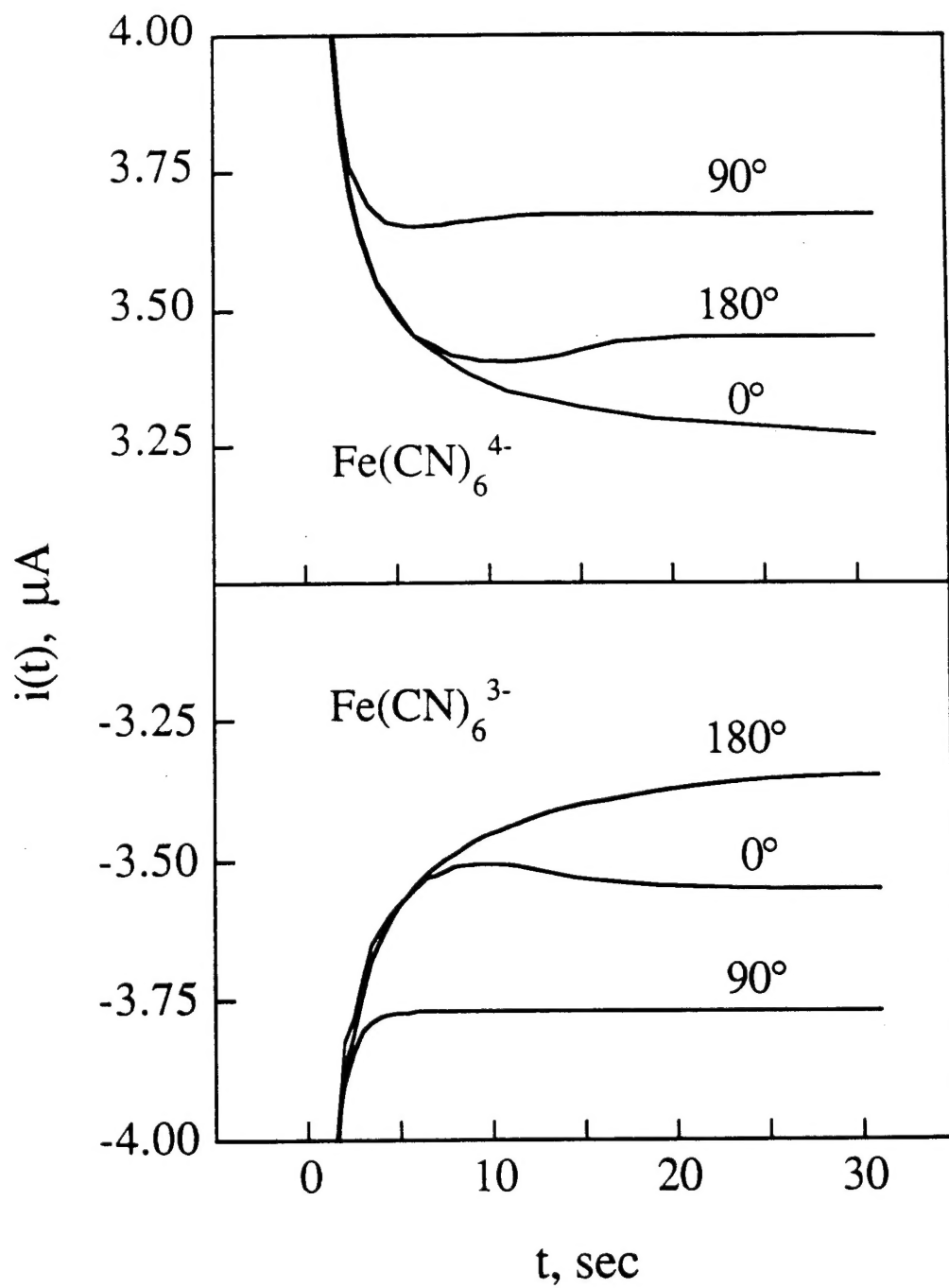


Fig.6